PATENT SPECIFICATION

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International Classification:—**C08f, g. D06p.**

COMPLETE SPECIFICATION

Process for Fixing Pigments on Fibrous Materials or Foils

We, FARBWERKE HOECHST AKTIENGESELLSCHAFT, vormals Meister Lucius & Brüning, a body corporate recognised under German law, of Frankfurt(M)-Höchst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is known that pigments can be fixed on fibrous materials or foils with the aid of an aqueous solution or dispersion prepared from natural substances of high molecular weight containing carboxylic groups, or polymers in conjunction with polyfunctional ethylene imine compounds. There have also been used for this purpose aqueous dispersions of polymers free from reactive groups, and aqueous solutions or dispersions of polymers containing reactive groups together with polyfunctional ethylene imine compounds or masked poly-isocyanates. It is also known to use a solution or dispersion of a substance of high molecular weight containing carboxylic groups in conjunction with a substance which under the action of heat reacts as a poly-isocyanate or liberates a free poly-isocyanate. It is also known that the disadvantages attendant upon the use of swellable thickening agents can be avoided by using oil-in-water emulsions as thickening agents. Consequently, oil-in-water emulsions have been used as thickening agents in the fixation of pigments on fibrous materials or foils by means of polymerization compounds which still contain reactive groups, or by means of polyfunctional compounds.

The present invention is based on the observation that pigments can be fixed on fibrous materials or foils in a manner which is especially resistant to mechanical treatment in the washing liquors, by applying to the fibrous material or foil from an aqueous bath or paste a pigment, an alkali-soluble resinous condensate containing reactive carboxylic acid groups and obtained by reacting a polycarboxylic acid with a polyhydric aliphatic alcohol, and a polyfunctional compound the functional groups of which contain a three-membered ring containing a nitrogen atom or an oxygen atom, drying the treated material, and then subjecting it to the action of heat, if desired, in the presence of steam.

If the resinous condensate is used in the form of a solution it is necessary for the bath or the paste to be weakly alkaline. If the resinous condensate is used in the form of a dispersion, however, the bath or the paste may be neutral or weakly alkaline.

The process according to the present invention may be modified by applying the polyfunctional compound to the fibrous material or foil before or after the padding liquor or printing paste containing the pigment and the resinous condensate containing reactive carboxylic groups.

In addition to the resinous condensate described above, there may also be added to the bath or paste another natural or artificial resin which may also contain reactive groups. There may also be added to the printing paste or the bath softening agents or agents accelerating the condensation.

As resinous condensates there may be mentioned, for example, incompletely condensed polyhydric alcohol-polycarboxylic acid reaction products which still contain free carboxy-

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by stirring the organic solvent into a previously prepared aqueous solution of the emulsifier, for example, an aqueous solution of a protein or hydroxyethylated compound. The emulsions may also be prepared by mixing, while stirring vigorously, an aqueous alkaline solution of the salt of the resinous condensate containing reactive carboxylic groups, which also acts as an emulsifier, in small portions with the organic solvent, if desired, in the presence of a protective colloid.

If the pigment padding process is to be used, it is not necessary in all cases to add a thickening agent to the padding liquors.

As pigments suitable for use in the process of this invention there may be mentioned, for example, inorganic pigments, such as titanium dioxide, zinc oxide, iron oxides, carbon black, ultramarine, lead colours, or metallic powders such, for example, as aluminium, copper or brass, either in the finely powdered state or in the form of lamellae or scales, and organic pigments, for example, vat dyestuffs, azo-dyestuffs and phthalocyanines.

As materials to be treated, there come into consideration, for example, sized or unsized paper, natural or regenerated cellulose fibres, acetyl-cellulose fibres, animal fibres for example, feathers, synthetic fibres of polyacrylonitrile, polyvinyl chloride fibres, polyamide fibres, polyester fibres, glass fibres, asbestos fibres, artificial leather and foils of all kinds.

The pigments are advantageously added to the bath or paste in the form of aqueous dispersions which may be prepared in known manner, for example, by triturating a pigment powder with a polyhydric alcohol, water and a dispersing agent. Such pigment dispersions may also be prepared by grinding an aqueous press cake of a pigment dyestuff with a dispersing agent, such as a fatty alcohol sulphonate, a cellulose ether or a water-soluble polymeric carboxylic acid, for example, polyacrylic or polymeracrylic acid, or salt thereof, or a condensation product of a naphthalene sulphonic acid derivative and formaldehyde.

A pigment dispersion prepared from a pigment powder generally contains the pigment in a coarser form than a dispersion prepared from a press cake, and this may often be disadvantageous in the printing process, for example, in that the pigments deposit in the engraving. On the other hand, a pigment dispersion prepared from a press cake of a pigment dyestuff with the aid of a dispersing agent has the disadvantage that the hydrophilic dispersing agent impairs the adhesion of the film of pigmented artificial resin to the support, especially if the film has to be repeatedly subjected to wet treatments. Moreover, the preparation of pigment dispersion from press cakes has the disadvantage that water-soluble impurities present in the water of the press cake, especially electrolytes, remain in the pigment dispersions and cause deposition of the pigment when they are worked up into printing pastes or padding liquors. When the known oil-in-water-emulsion thickenings are used, the content of electrolyte often impairs the stability of such emulsion systems.

These disadvantages inherent in known pigment dispersions can be overcome by adding to the dye bath or printing paste a pigment dispersion prepared by mixing the resinous condensate containing reactive carboxylic groups with the aqueous press cake of a pigment dyestuff in a neutral or acid medium, if desired, at a raised temperature, mechanically treating the mixture so obtained, removing the water which separates out, and treating the resulting pigment preparation with an alkaline liquid, preferably with aqueous ammonia.

In addition to their excellent stability and resistance to cold, pigment dispersions so prepared have the advantage that printing pastes made up with such dispersions do not tend to deposit in the engraving of the roller nor to clog the stencil gauze. Owing to the very fine dispersion of the pigment there are produced stronger and purer prints and dyeings, and owing to the absence of large amounts of hydrophilic auxiliaries prints and dyeings of better fastness to washing.

The aqueous alkaline solution of the resinous condensate containing reactive carboxylic groups present in the above pigment dispersion acts both as a dispersing agent and binding agent for the pigment. However, this does not preclude the use in certain cases of these pigment dispersions in admixture with additional substances, for example, an emulsifier. Such an addition is especially desirable when oil-in-water-emulsion thickeners are used in the dyebath or paste. However, it is always possible to use substantially smaller amounts of additional substances such as emulsifiers than are required with pigment dispersions other than those used in the present invention.

A further binding agent may be added when the pigment dispersion is worked up into a printing paste or dye bath. For this purpose there may be added an aqueous alkaline solution of the resinous condensate containing carboxylic groups already present in the pigment dispersion or a corresponding solution of another acid resin. Finally, there may be added other natural or artificial film-forming substances, which may or may not contain reactive groups, provided that such substances are compatible with the alkaline aqueous paste present.

In the process of the present invention, the pigment used may be "fibre dust," that is to say finely cut dyed textile fibres.

The process of this invention may also be carried out, for example, by first dyeing the entire fibrous material or foil uniformly with the above pigment composition of the invention, then printing thereon a single colour or multi-colour pattern with a printing paste con-

Composition of the Printing paste:

830 parts of the stock paste described above are stirred by means of a rapid stirrer with

100 parts of an aqueous solution of 30 per cent strength of the reaction product of 1 mol of hexane-1:6-diisocyanate and 2 mols of ethylene imine, and to the resulting mixture are added

70 parts of a ground paste of 25 per cent strength of the red azo-dyestuff No. 86 described in Schultz, Farbstofftabellen, 7th edition.

1000 parts

With the printing paste so obtained a fabric of polyamide fibres is printed, dried and then fixed either by a short steaming operation or by a heat treatment at 100°—150°C.

EXAMPLE 3.

A fabric of lustrous cuprammonium rayon is padded with a padding liquor prepared as follows:

200 parts of an ammoniacal solution of 30 per cent strength of an alkali-soluble alkyd resin obtained by condensing for 8 hours at 170°C. 0.9 mol of glycerine and 0.1 mol of 1:4-butylene glycol with 0.8 mol of phthalic anhydride and 0.35 mol of adipic acid in the presence of a small amount of boric acid, the condensation being carried out in such a manner that a product still soluble in alkali is obtained,

100 parts of an aqueous solution of 4 per cent strength of the sodium salt of cellulose glycollic acid,

100 parts of an aqueous dispersion of 40 per cent strength of a copolymer obtained from vinyl acetate, acrylic acid butyl ester and acrylic acid,

30 parts of ammonia solution of 25 per cent strength,

35 parts of the reaction product of 1 mol of propyl disulphochloride and 2 mols of ethylene imine, and

250 parts of a paste of 40 per cent strength of titanium dioxide are made up to

1000 parts by volume by the addition of water.

After drying the fabric, the dyestuff is fixed as described in Example 1 and 2. A matt effect of good fastness to washing is produced.

EXAMPLE 4.

A solution is prepared which consists of 50 grams of a solution of 25 per cent strength of ammonium caseinate, 60 grams of water, 10 grams of 1-ethoxy-2-acetoxy-ethane (ethylglycol acetate), 20 grams of an aqueous solution of 30 per cent strength of an alkyl-aryl sulphonate, 0.3 gram of sodium pentachlorophenolate, 5 grams of diethanolamine, 5 grams of an aqueous solution of 50 per cent strength of ammonium thiocyanate and 10 grams of urea.

In the solution so prepared are emulsified by means of a rapid stirrer 440 grams of a solution of 5 per cent strength of polyisobutylene in a petroleum fraction having a boiling range of 170°—220°C. Into 600 grams of the highly viscous paste so obtained are introduced, while stirring, 250 grams of a dyestuff paste consisting of 12 parts of the yellow azodyestuff obtainable by coupling diazotised 2-nitro-4-chloraniline with 2-chloracetoacetic acid aniline, 30 parts of the alkali-soluble alkyd resin described in Example 2, 5 parts of ammonia solution of 25 per cent strength and 53 parts of water.

To the paste so obtained are finally added, while stirring, a further 70 grams of an aqueous solution of 50 per cent strength of the reaction product of 1 mol of phosphorus oxychloride with 3 mols of ethylene imine and 80 grams of water, whereby 1000 grams of a smooth mobile printing paste are obtained.

A fabric of regenerated cellulose is printed with this printing paste, dried and steamed for 3—5 minutes in the rapid ager. A brilliant yellow print is obtained of a good fastness to washing and light.

EXAMPLE 5.

One part of the printing paste described in Example 4 is diluted with 3 parts of water, and mixed with 1/25 part of an alkyl-aryl sulphonate. A fabric of poly-acrylonitrile fibres is padded with the solution so obtained, dried and then heated for 10 minutes at 150°C.

EXAMPLE 6.

The printing paste described in Example 4 is printed on a cotton fabric without the addition of the reaction product of 1 mol of phosphorus oxychloride with 3 mols of ethylene imine, and the printed fabric is then padded with an aqueous solution of 5 per cent strength of the reaction product of 1 mol of the tri-isocyanate of 1:3-dimethyl-2:4:6-triaminobenzene with 3 mols of ethylene imine. The fabric is dried and then steam for 5 minutes in a rapid ager.

EXAMPLE 7.

550 parts of a solution of 10 per cent strength in butyl acetate of an alkali-soluble alkyd resin obtained by condensing 1 mol of hexane-triol-(1:3:5) with 1.2 mols of phthalic anhydride are introduced, while stirring, into 350 parts of an aqueous solution of 6 per cent strength of sodium lauryl sulphonate, whereby a mobile dispersion of the resin is formed.

50 parts of a paste of 30 per cent strength obtained by grinding iron oxide in butyl acetate are then added and, after the addition of 20 parts of the reaction product of 1 mol of diethyl oxalate with 4 mols of ethylene

an ammoniacal solution of 40 per cent strength of the condensation product prepared from 1 mol of hexane-triol-(1:3:5) with 1.2 mol of phthalic anhydride, 1 part of ammonium thiocyanate, 10 parts of an alkyl-aryl polyglycol ether, and 79 parts of water.

Composition of the Printing paste:

200 parts of the pigment dispersion obtained as described in Example 1 of Specification No. 801,522 (containing 15 per cent of Hansa yellow G, G. Schultz, Farbstoff-tabellen, 7th edition, No. 84, 30 per cent of the condensation product, in the form of the ammonium salt, prepared from 1 mol of hexane-triol-(1:3:5) and 1.2 mols of phthalic anhydride and 55 per cent of water) are stirred with
700 parts of the emulsion described above,
25 parts of a solution of 80 per cent strength in toluene of the reaction product of 1 mol of phosphorus oxychloride with 3 mols of ethylene imine
25 parts of a solution of 10 per cent strength in benzene of the reaction product obtained by reaction of 1 mol of phosphorus thiochloride with 3 mols of ethylene imine in the presence of an acid-binding agent, and
50 parts of water.

1000 parts

A fabric of staple fibres of regenerated cellulose is printed with the mobile printing paste so obtained by machine printing, dried and then steamed for 5 minutes at 70° C. in a rapid ager. A brilliant yellow print is obtained of good fastness to washing and light.

EXAMPLE 13.

An oil-in-water emulsion is prepared as follows: 650 parts of a petroleum fraction having a boiling range of 190°—220° C. are introduced, while stirring, into an aqueous solution of 100 parts of an ammonium caseinate solution of 25 per cent strength, 10 parts of an alkyl-aryl polyglycol ether, 130 parts of an ammoniacal solution of 30 per cent strength of a copolymer of 90 parts of vinyl propionate and 10 parts of crotonic acid, and 110 parts of water.

Composition of the Printing Paste:

130 parts of a pigment dispersion obtained in a manner analogous to that described in Example 1 of Specification No. 801,522 (containing 12 per cent of copper phthalocyanine blue, 30 per cent of the condensation product, in the form of the ammonium salt, prepared from 1 mol of hexane-triol-(1:3:5) and 1.2 mols of phthalic anhydride, and 58 per cent of water) are mixed with
650 parts of the emulsion described above,
100 parts of diglycide ether and
120 parts of water.

1000 parts by volume

With the printing paste so obtained a cotton fabric is printed, dried and then heated for 10 minutes at 150° C. A blue print is obtained of good fastness to washing.

Instead of 100 parts of diglycide ether there may be used 100 parts of di-epoxy-butane. A cotton fabric printed with the printing paste so obtained is dried and steamed for 7 minutes at 101° C. with saturated steam. A blue print is obtained of good fastness to washing.

EXAMPLE 14.

100 parts of an aqueous pigment paste of 20 per cent strength of the yellow dyestuff obtainable by coupling diazotized 2-nitro-4-chloraniline with 2-chloroaceto-acetic acid anilide are stirred with
300 parts of an ammoniacal solution of 30 per cent strength of the condensation product obtained from 1 mol of hexane-triol-(1:3:5) and 1.2 mols of phthalic anhydride,
350 parts of an aqueous dispersion of 50 per cent strength of polyvinyl acetate in a fine state of dispersion,
70 parts of an aqueous dispersion of 50 per cent strength of polyvinyl propionate in a coarse state of dispersion,
30 parts of triethanolamine.
20 parts of potassium sulphite solution of 45° Bé
100 parts of the oil-in-water emulsion described in Example 9, and
30 parts of an alcoholic solution of 90 per cent strength of the reaction product of 1 mol of phosphorus oxychloride with 3 mols of ethylene imine,

1000 parts

A cotton fabric, which has been pretreated with a padding solution of aniline black of the usual composition, is printed with the above printing paste, then dried and subjected for 7 minutes at 101° C. to the action of saturated steam. The printed fabric is then after-treated for about 30 seconds at 60° C. with 3 grams

rinsing and soaping for a short time at 40—60° C.

WHAT WE CLAIM IS:—

1. A process for fixing pigments on fibrous materials or foils wherein an aqueous bath or paste containing a pigment, an alkali-soluble resinous condensate containing reactive carboxylic acid groups and obtained by reacting a polycarboxylic acid with a polyhydric aliphatic alcohol, and a polyfunctional compound the functional groups of which contain a three-membered ring containing a nitrogen atom or an oxygen atom, is applied to the fibrous material, the bath or paste being weakly alkaline when the resinous condensate is used in the form of a solution and being neutral or weakly alkaline when the condensate is used in the form of a dispersion, and the treated material is dried and then heated.

2. A modification of the process claimed in claim 1, wherein the treated material is heated in the presence of steam.

3. A modification of the process claimed in claim 1 or 2, wherein the polyfunctional compound is applied to the fibrous material or foil before or after the padding liquor or printing paste containing the pigment and the resinous condensate containing reactive carboxylic groups.

4. A process as claimed in claim 1, 2 or 3, wherein the functional groups of the polyfunctional compound are ethylene imine or alkylene oxide radicals.

5. A process as claimed in claim 1, 2, 3 or 4, wherein the paste contains as a thickening agent a substance capable of swelling in water.

6. A process as claimed in claim 1, 2, 3 or 4, wherein the paste contains as a thickening agent an oil-in-water emulsion containing as the inner phase an organic solvent which is immiscible or sparingly miscible with water.

7. A process for fixing pigments on fibrous materials or foils conducted substantially as described in any one of the Examples herein.

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